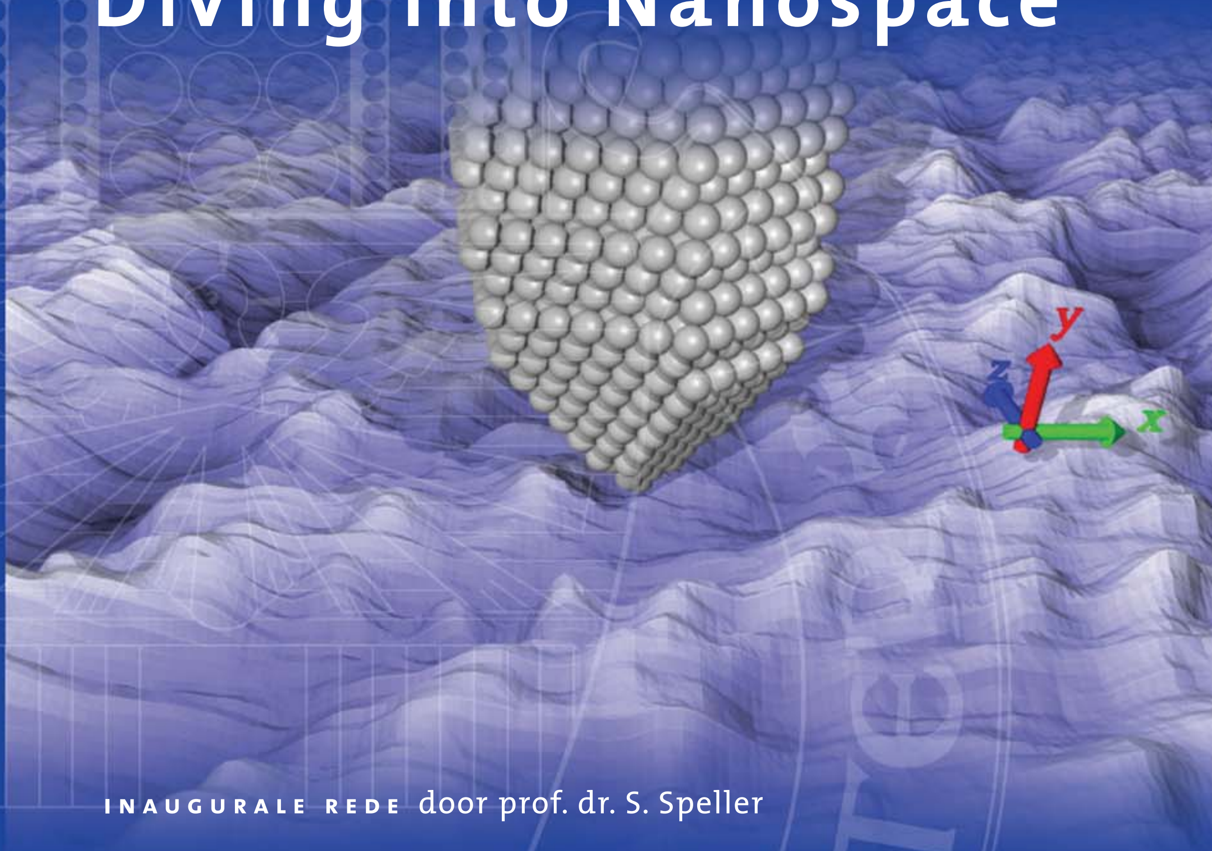
Diving into Nanospace



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Mijnheer de Rector Magnificus,
dear ladies and gentlemen,

Nanotechnology

"There is plenty of room at the bottom", by this sentence Richard Feynman, US physicist and nobel prize winner, was heralding the era of nanotechnology. In his famous talk 44 years ago [1] on the annual meeting of the American Physical Society at Caltech he formulated an invitation to enter a totally new field of physics. Feynman was the first who was envisaging that fabrication in the nanometer area is principally feasible. In his opinion it should be possible to tailor material properties, produce novel computers of nano elements, write by electron beams, and store the complete encyclopedia in the tip on a head of a pin. Many of the listeners believed he was only joking.

Assembler

20 years later the idea was taken up further by the physicist and computer specialist K Eric Drexler. He is founder of the Foresight Institute and he is probably the most famous and debated nanotechnologist so far. In his book *Unbounding the future* [2], he describes a future where tiny nano-robots, so called assemblers, produce all kind of things needed, including new robots and machines, that are acting intelligently and independently from men. Such way, society could get rid off any problem, hunger, cancer, rubbish piles, and scarceness of resources. Drexler also co-founded the company Zyvex, that aims to produce an universal automatic assembler-based construction kit, that shall fulfill the wishes of the users. The feasibility of their superambitious plans is questioned among experts. In return, Zyvex simply points out the existence of natural self-assembling-machines, for instance a cow for the fabrication of milk and steak, out of grass and light.

One example from their research is mechanical erythrocytes, nanorobot-based artificial red cells, that would redundantize breathing [3] (Figure 1).

Funding

The important position of nanotechnology in the US is partly due to Drexler's testimony during a senate hearing on *New Technologies for a Sustainable World* in 1992. This was two years after Eigler's research group had spelled 'IBM', manipulating 35 xenon atoms individually [4]. Western government's advisors regard nanoscale science and engineering as *the* field that will produce the breakthroughs of tomorrow and lead to the next industrial revolution. Currently, US is supporting nano-research with $ 850 million (2003). Also other technologically oriented nations, like Japan, the European Union, and South Korea, support nanoscience and -technology substantially. The global nano-related funding is estimated at $ 4 billion this year.

Revenues

But how big is the current nano market and how much will it grow in the immediate future? According to Deutsche Bank, pure nanotech products, such as nanopowders or nanostructured materials, currently generate revenues of approximately $ 22 billion worldwide. The biggest benefactors of this business are chemical companies. However, nanotechnology does not represent an independent industry, and one has also to take into account final products that are impacted by it. Thus the calculated world market for products that contain nanocomponents, such as computer hard disks and displays, amounts to more than $ 100 billion growing at an annual rate of about 20%. This estimate appears balanced compared with calculations from the Verein Deutscher Ingenieure (VDI) and the Nano Business Alliance (NBA). A saturation is not expected before mid of this century.

Popularization

Certain problems are beyond nanotechnology's power to solve; exaggerated scenarios are disseminated in media and fiction. One can read in the popular press about an imminent future, with tiny submarines patrolling our bodies, stitching up damaged tissue, eliminating an occasional cancer cell or virus, or switching off errant genes; nanorobots weaving extensions to our brains to enhance our intelligence; desktop machines that can produce diamonds; a table that will transform into a chair at the flick of a remote control; mind-reading, and immortality [5].

Prey is a novel that triggered public discussion about nanotechnology as a danger [6]. In the story a company, leading in Molecular Manufacturing created self-replicating nanoparticles that behave 'emergent'. They can form a medical nano camera that works like a de- and reassembling compound eye and that can enter the finest vascular systems. A specialist in 'emerging behavior' of artificial agents can hardly save the world from the particle 'swarms', as they undergo generational evolution and mutations quickly.

Threat?

Societal risks are indeed linked to scientific research and people feel increasingly threatened by nuclear power, bio-terrorism, information awareness, genetic engineering, clone copies, robotic attacks, and genetic discrimination.

Do it yourself virus

Following a recipe, downloaded from the web, and using synthetic gene sequences from a mail-order supply, researchers have assembled a manmade version of the polio virus [7]. They injected it into mice, who became paralyzed and then died. This proved that it is possible for terrorists to make deadly biological weapons. Experts do not exclude synthesis of the smallpox virus, although that is much more difficult. Debates are started to put censorship on scientific results to avoid sensitive knowledge coming into wrong hands. The US government added a new category of materials "sensitive but unclassified" (SBU) under that come all information that 'possibly' could be used for the production of weapons of mass destruction, and publication is withheld.

Information Awareness

The research department of the pentagon DARPA was planning a sweeping computer surveillance system named Total (later Terror) Information Awareness to defeat terrorists by tracking and analyzing huge amounts of data – from traveling, educational to financial and biometric information. Similar to the one-dollar-bills the offices' logo contains the controversially discussed eye on pyramid symbol from the great seal of the US. This program had to be partly revoked recently.

First nanoproducts

What are current examples of nanoproducts?

- *Nano edible oil:* The anti-microbial nano-emulsions of the company NanoBio are water-oil emulsions that employ uniformly sized droplets in the nanometer range.

The nano-emulsions destroy microbes effectively without toxicity or harmful residual effects. The classes of microbes eradicated are virus (eg., HIV), bacteria, spores (eg. anthrax), and fungi.

The mechanism is as follows: At a droplet size below 400 nm the surface tension of the drops rises precipitously. The tinier the oil drops, the larger is this effect. The oil balls resemble liquid bombs. When they come into contact with bacteria or viruses, the agents are destroyed at the surfaces of their membrane - lipids or proteins - which brings the tension-loaded drops to explode.

- *Nano ski wax:* The enterprise Colloid Surface Technologies GmbH introduced Cerax Racing polymer, an efficient coating for ski and snowboards based on self-organizing nano-structures. The German national team, as well as Swiss and American ski runners use this coating. It is rumored that the wax caused a number of world champion titles. Also Graffiti resistants on the same basis outperform conventional products on the market, in environmental compatibility.
- *Lotus coating:* Most known is the Lotus effect, an anti adhesion system copied from nature. At the University of Bonn it was noticed that from the leaves of the Lotus flower, considered holy in Asia, even honey is dripping off, leaving the leaves clean. Lotus coatings are used as paints and glazes.
- *Nano diamond:* By the plasma polish process developed at the Gesellschaft für Diamantprodukte it is now possible to produce cutting edges which are only few nanometers large. That means that only few atoms form the cutting edge, thus a physical border is reached. Together with microstructuring procedures microscopically small blades, which are only little broader than a human hair can be produced. The use of this technology for diamond scalpels in the micro surgery shows that subjectively force-free cutting is possible. Improved precision and the reduced damage of the surrounding tissue is reached.
- *Capsule Endoscopy:* 'A camera pill' allows physicians to image the small intestine with high precision. The diagnostic system was cleared as a first-line tool in the detection of abnormalities of the small bowel.
- *Magnetic fluid hyperthermia:* The company MagForce produces iron nanoparticles that are used in a tumor-specific hyperthermia therapy, developed at the Charité Berlin [8]. The particles are injected as magnetic fluid and get primarily resorbed by the tumor cells. Cancer tissue is selectively heated up by coupling alternating current magnetic fields to the targeted magnetic fluids.

- *RFID tags:* The European Central Bank is working on embedding radio frequency identification tags into paper money. These are wireless transponders not bigger than a grain of sand, that can be embedded into the fibers of bank notes to foil counterfeiters. The market for miniaturized tags is incredibly large and some of the applications are worrying.
- *Biological-technical hybrids:* First biological technical hybrid systems are produced. They inhere biogenic hardware for power supply, locomotion, perception, and navigation. Robotic insects will be used for spy jobs, among other.

One billionth

One nanometer is tiny a billionth of a meter. A spherical molecule of 60 atoms is large one nanometer. A soccer ball is 10^9 times larger, Jupiter is again 10^9 times larger than a soccer-ball (Figure 2).

Bottom-up

Nanotechnology cannot continue just miniaturize things like in the past decades, but requires the development and implementation of totally new fabrication concepts. The microstructures in our current electronics are predominantly produced by so-called top-down techniques, that is, material is etched or eroded away and the remainder gives the desired structure, like carving sculptures. Nanotechnology is done in a bottom-up fashion, that is, by controlled assembly of molecular and atomic building blocks.

This applies to solid and soft matter. Atomic adsorption can be used to spontaneously nanostructure a surface, or supermolecules can be synthesized from smaller units. In contrast, present days microelectronics chips is structured mostly by optical lithography, a typical top-down technology. This needs a mask being aligned onto a photoresist layer on the semiconductor, and exposure to ultraviolet light. The soft-matter top-down analogue is the isolation of bio-molecules from biologic tissue.

Nanoprobing

How to dive into nanospace ?

Dealing with such small dimensions humans are blind. It is impossible to see nano-objects by light, because visible light is 500 times too coarse. Second, with conventional electron microscopy the spatial resolution is too poor, and imaging is limited to special environments. Another problem is that electron microscopy does not yield quantitative topographies, the image is only quasi three-dimensional, like what we see with our eyes. In the nanoscopic world this represents a stronger constraint, because one cannot simply walk around the objects, or use experience. A number of in principle powerful nano-analytical methods exist, but they come with deficiencies with respect to nanosystems: Average signals are taken and characterization is only indirect. Nanosystems are aperiodic and inhomogeneous and require local visualization and manipulation in real space on nanoscale, which is provided exclusively by Scanning probe microscopy (SPM) so far.

Scanning probe microscopy

An eventually helpful way to think of the SPM probe is a finger reading Braille, or a gramophone needle playing a gramophone record — with one important difference: the nanoprobe usually does not physically touch the surface (Figure 3). This is managed by mounting the probe on actuators, capable of nanometric precision. These are adjusted according to a signal stemming from a local interaction between tip and sample. The nanoprobe is scanned over the surface and the signal is maintained constant by means of a feedback circle. In this way, surface characteristics, for instance, the topography of a surface is mapped that shows terraces and steps.

Individual atoms can be seen routinely, if the surface is prepared reasonably flat. Figure 4 shows the topography of a chemically alloy of platinum-tin. But only one species is visible by STM, the other is invisible. This is the highest so-called chemical contrast one can obtain. Furthermore, the topography shows vacancies. At room temperature they are mobile with time constants of minutes. This can be observed in movies or successively taken sets of images.

Scanning Tunneling Microscopy also allowed nanoscopic characterization of defects, for instance screw dislocations. Dislocations are very important defects with regard to the ductility of a material. They wander when the material is deformed but can get pinned by impurities, such that the shape is taken irreversibly with impure metal, in contrast to pure metal.

Idealization

Such images are charming but one must have in mind that they have been taken under largely distortion-free conditions. First, the samples are mono-crystals, whereas most natural minerals occur in polycrystalline form. Second, they have been prepared by ion-bombardment and subsequent annealing, and third, to avoid contamination (which would foil proper imaging) a vacuum was used that is better than at most interplanetary places, that is 1 nanoPascal or 14 orders of magnitude below atmospheric pressure. The next collision partner is about 10^8 meters away and it will take days till a complete monolayer has adsorbed onto a surface.

Tunneling

The first interaction used to prevent the nano-probe crashing into the sample was quantum-mechanical tunneling of electrons. So-called tunneling is a very common phenomenon: There is appreciable transmission from a wave across an actually 100 % reflective barrier if the thickness compares to the wave length. The reason for this effect is that discontinuities are unphysical. For instance light beams cannot be flipped precisely in front of a mirror but must enter the material by a fraction of its wave length. If the reflective coating is thin enough, light is transmitted.

The tunnel current I turned out to be very sensitive to the local distance z, thus is optimally suited to control the distance in a feedback system. Experimentally, electron tunneling was evidenced only in 1971 [9].

Early in the last century, quantum mechanics was young, and it was surprizing how universally wave concepts do apply. Transmission of electrons through energetic barriers appeared strange and was denoted ‘tunneling’, although this name is only correct in the metaphorical sense. The effect applies to all kind of waves coming across thin barriers, for instance, water waves over narrow abysses, light across totally reflecting but thin materials, and electrons across insulating gaps.

Nanoprobing methods

In 1986 Binnig and Rohrer were awarded the Nobel Prize for the invention of scanning tunneling microscopy (STM) [10].

Since then, many new types of scanning probes microscopies, using other local interactions, like forces and light tunneling, have been developed, such that it became possible to image on insulating materials and to probe a wealth of properties, beyond topography, for instance local electron spectroscopy, work function, vibrations, elasticity, friction, magnetic, and optical properties. This is a research area where experiments are clearly ahead of theory. Nanometric contrasts are observed, the origin of which is yet unsolved and that demand for theoretical description.

Nanostructuration

How to build a nanostructure?

At this early stage it is convenient to work on a surface. There are two principally different ways to produce nanostructures: nanomanipulation by scanning probes or highly focused particle beams allow to write nanostructures very precisely, but is inherently slow. Self-structuration is parallel, thus fast, but so far less controllable. Future nanodevices will include elements of both types, nanostructure arrays with uniform sizes and spacings and individually written structures.

Quasi-natural nanostructures

Already the atomic arrangements within crystals represent ordered natural nanostructures. But only if such a structure can be tailored this represents a step forward towards nanotechnology. In the case of the anisotropic low-index platinum surface the reconstruction comes together with a mesoscopic step net structure called 'fishscale pattern'. This is an equilibrated structure and the reconstruction originates from the lower energy of the densely packed microfacets at the ripples flanks, and from surface stress. The fishscale step pattern serves to hide antiphase domain walls in order to lower the energy of the system. On face-centered-cubic(110) surfaces the pattern is not present with reconstructions other than (1x2), for example it disappears if the Pt(110) surface takes a (1x4) reconstruction.

Adsorption can be used to lift or induce such reconstructions. Electron accepting species, like oxygen or sulfur, decoarsen or deconstruct the surface while an initially unreconstructed surface will coarsen upon adsorption of electron donating adsorbates like hydrogen, carbon monoxide, and ethylene. Adsorbates alter the balance between delocalized s electrons that tend to extend the interatomic distance, and the d type electrons that rather tend to compress the lattice.

Steps

A practical way to produce an anisotropic surface is using steps. Steps can be produced purposely applying a certain miscut (wedging) with respect to a low-indexed plane of a monocrystal. The discrete structure results in stepped or so-called vicinal surfaces. Interestingly, the steps tend to arrange themselves in an ordered array. This ordering is due to repulsive interaction of electronic dipoles and strain fields, linked to the steps.

The energy around a step is higher due to missing neighbor atoms. This leads to fluctuations which are pronounced already at room temperature with low-melting metals. The STM is not fast enough to take a snap-shot of the area, the topography is undersampled in time, and temporal and spatial information gets mixed. In consequence, the steps appear frizzled.

Additionally, the steps are rather prone to forces present when the tip is close-by. The closer the tip the stronger the step atoms are pulled by local forces due to tip-surface interaction and enhanced frizziness is observed.

On the other hand, the extent of the fluctuations depends on the atomic structure of the steps. The more broken bonds, the stronger the fluctuations become.

Fluctuating systems are more difficult to image and in this case atomic structure is only indirectly perceivable. When measuring the terrace width distribution it turns out that it is quantized, peaking at widths corresponding to integers of atomic rows.

Nanostripes

Such step arrays do represent not only geomatic nanostructures, but also electronical. Remarkably, upon adsorption of silver the step array breaks up into two phases: well-matched adsorbate-covered facets and adsorbate-free stripes (Figure 6). This hill-and-valley structure has a period of around 10 nm and an amplitude of 1 nm. The period can be tuned via the Ag coverage. The topography of the Ag stripes allows to deduce a Moiré pattern of a quasi-hexagonal Ag(111) adlayer rotated by 5.2 degree versus a steeper underlying Cu facet of (223) orientation. The facets' slope is larger than the average, and consequently, with increasing coverage, the remaining Cu regions become depleted in steps, until the last one has been taken [11].

It is not directly clear what governs the period of such spontaneously formed nano structures. In this case the dependence of the period on the coverage is characteristic, such that it can be attributed to concurring interactions. The energy balance contains a negative border energy and a repulsive interaction between two domain boundaries. Energy minimization with respect to the coverage yields a theoretical behavior of the domain width and period with coverage, as depicted here. A comprehensive quantitative analysis of the system is unambitious. It allows to conclude stress being relieved by the rippling, induced by the Ag.

Anisotropic surface stress plays a crucial role in nanostructure formation. Sometimes, even the pure surface spontaneously ripples. Due to the lower coordination, solid surfaces are mostly under tensile(positive) stress, thus they would prefer to adopt a smaller lattice spacing but the underlying bulk lattice prevents compression. Liquid surfaces have zero lateral stress because there is no resistance to a flow of atoms, and the surface atoms can adjust their spacing quasi-freely.

More important, such structures show striking nanoelectronic signatures. In this case we analyzed the electronic structure using photoemission and found that electron waves on Cu get strongly confined in-between the wires. A new one-dimensional Ag-related nanoelectronic state was discovered. STM is also capable of local electron spectroscopy. Scanning tunneling spectroscopy is very powerful, but yet still less straightforward because the electronic structure of the tip is insufficiently known.

Nanodot arrays

Wires represent only one type of low-dimensional geometry, likewise important is physics of nanodots. There are only a few ways to produce ordered arrays of dots; mostly they rely on the interaction of a deposited species onto a nano-templated substrate. In this direction we are trying to produce hexagonally ordered arrays of Cobalt nanodots, and to understand the underlying mechanisms.

Alloy surfaces accumulate substantial stress during preparation. This is due to the ion-bombardment used for cleaning. The efficiency atoms are removed depend on the atomic mass. The surface region becomes depleted in the lighter atomic species and the composition can not be restored via diffusion at intermediate temperatures. Depending on the difference of the atomic sizes the lattice can relieve stress by introduction of extra planes, edge dislocations. The lines where the planes meet the surface appear elevated by about 1/20 nm. The reason is the locally higher electron density. The subsurface dislocation network orders to reach optimally distributed stress relief. This is a metastable structure and the equilibration is ahead in the center of the honeycombs of the structure. The dislocation lines indeed affect nucleation and growth of deposited material as can be seen in the topography (Figure 7, left). The islands in the center of the honey combs are systematically smaller and denser (Figure 7, right).

Processes on nanoscale

Oxidation

It would be very fascinating and elucidating to watch a chemical reaction, for instance, an oxidation, on-line and in real space. If a clean surface is exposed to oxygen it depends on its reactivity how thick the oxide layer becomes. The image (Figure 8, left) shows a monolayer adsorbed on a metal surface during annealing. The corrugation is pronounced and one is tempted to attribute the protrusions to adsorbed oxygen. This is however one of the typical pitfalls in STM. The protrusions show just places in-between of adsorbed oxygen. Oxygen reduces the the electron density and is often imaged as depression [12]. Oxides are effective catalysts and are used in gas sensors.

Due to its simplicity the carbon monoxide oxidation represents a basic model reaction. It is of practical importance for the control of environmental pollution that results from combustion processes. On the clean surface the adsorbate layer does never complete. The molecules are standing upright with the carbon towards the surface. They tend to form dimers and tetramers. The mobility is moderate and can be reasonably followed by STM. This is an exceptional situation with adsorbed CO, usually exhibiting high mobility (Figure 8, right). Superposition of successive images, differently colored, allows to monitor changes. At red an green positions molecules left or arrived. Statistical analysis allows to conclude that freshly adsorbed CO primarily occurs as monomers. New dimers need one preadsorbed and one freshly adsorbed monomer to be formed. Dimerized CO is immobile.

If both, oxygen and CO, are adsorbed on the surface, the phases simply coexist, the CO is not oxidized in appreciable amounts. Obviously, the UHV environment is not suitable to obtain a direct reaction of oxygen and CO, in contrast to the situation for electro-oxidation in acids. The oxygen is simply not available. CO poisoning effects should be lower on the alloy surface than on pure Pt. Due to the so-called pressure and material gaps the results are not directly transferable to realistic catalytic conditions.

Increasing Complexity

As mentioned above, these surfaces were prepared and measured under ultra-high-vacuum (UHV) conditions. It took decades to realize these idealized experiments and to accumulate fundamental understanding. It is however of eminent importance to include more practical and physiological conditions, but this time on the solid basis of atomic level understanding. In the following, steps towards ambient and liquid environments and towards molecules with increasing size and complexity, eg, organic, super- and biological molecules are presented.

Liquid STM

The Nijmegen ambient STM is a home-built, pocket-size, easy-to-operate, instrument. It was constantly improved over the years. The instrument is such user-friendly that every week first year students and even high school pupils obtain molecular contrast [13]. This STM was the basis for our controlled atmosphere experiments, and liquid STM (Figure 9, left).

Liquid STM is hard to perform. First, molecules evaporating from the liquid flurry the environment leading to local drift, secondly, the nature of the electric tunnel current and tip-surface interaction is more complex. Another problem is that the sputter-anneal preparation, as performed in UHV, is no longer possible. One has either to cleave a monocrystal directly in the liquid or to use inert surfaces, like graphite. Furthermore, the liquids must be thoroughly cleaned.

Finally, diffusion is enhanced because it is no longer limited to two dimensions. The latter is the reason that the STM topography of the Bi(111) surface only shows noise. The phenyloctane molecules used here do not adsorb on the surface. When admitting adsorptive molecules, like octanethiols, the surface dynamics gets decelerated with increasing coverage. Thiols are the sulfur analogues of alcohols. Two amino acids, cysteine and methionine, contain thiol groups. The sulfur group sticks to metal surfaces and the surface gets locally pinned upon thiol adsorption. After a while a self-assembled monolayer of upright standing molecules has completed, and imaging becomes stable.

Nanomachining

These images were taken at comparably low setpoint currents. Using somewhat lower tunnel resistances results in stronger tip-surface interaction, accompanied by etching of the Bi surface (Figure 9, right). The local etching is interesting from point of view of nanomachining. It is plausible that the Bi atoms are dissolved and carried away as Bi-thiol complex.

Molecular Assemblies

Porphyrins

Thiols and alkanes are yet rather simple chemical groups. In collaboration with organic chemists we study the adsorption of porphyrins and superporphyrins. Porphyrins have heterocyclic structure and are active parts in hemoglobin and chlorophyll. In hemoglobin oxygen can bind to the Fe center of the porphyrin and is transported to the tissues. In chlorophyll the central ion is magnesium bound to four nitrogen in a square arrangement. Chlorophyll is capable of converting the energy of sunlight into chemical energy through the process of photosynthesis.

The porphyrin we use here is empty (no metal center), but has four hydrocarbon chains attached. This is an artificial type of porphyrin that has been synthesized by organic chemists. Adsorption leads to a self-assembled two-dimensional monolayer with horizontally arranged molecules. If one tries hard, faint holes can be recognized in the centers. The contrast is sub-optimal, in particular the assembly appears loose and molecules do wobble around their average position. This adsorption is only weak, referred to as physisorption, in contrast to the stronger chemisorption.

The imaging contrast substantially improves if a jelly environment is used. Adsorption remains weak, but apparently the gel effects a resistance to movement of molecules. In the topography the hydrocarbon chains stay invisible, simply because the porphyrin rings have higher conductivity.

Fatty acid

Stearic acid is a saturated fatty acid and most common, for instance, in food. Fatty acids are hydrocarbon chains with a carboxyl group at one end. These molecules assemble in a layer with sideways adsorption geometry (Figure 10). The arrangement of the molecules is such that two carboxyl groups oppose and form a double hydrogen bridge. The hydrogen bridge is imaged as depression in-between hydrocarbon but in very clean non polar media the contrast reverses. Hydrogen bonds are flexible and very important in nature, e.g. during replication of DNA they need to be opened and fastened constantly.

An aggregation of similar type leads to the formation of biological membranes. The hydrocarbon chains dislike polar media, while the carboxyl does like water. Thus many lipids spontaneously form bilayers that stack into sheets (multilamellar bilayers). Enigmatically, the formation of *single* bilayers, that constitute cell membranes, is critical. Although the thickness of only 8 nm we are *not* able to perform STM on a complete cell membranes with our current instruments, owing to the low conductivity of the unconjugated hydrocarbon.

Molecular architecture

Nevertheless, we reached a clear step towards high resolution imaging of thick molecules, by enabling ultrasmall tunnel currents, below one picoAmp. This porphyrin hexamers are synthethized from porphyrin units [4] and take a disk-like structure. Aggregation on the surface only takes place at slow rate. Ordered patches show up, and increasingly replace disordered areas (Figure 11). The disordered areas show no molecular contrast, because molecules are in a quasi-liquid state yet.

The question is what kind of structure the aggregate takes and whether we are able to switch the supramolecular structure. Initially, the molecules adsorb in a face-on geometry, at least this is most compatible with the observed STM topographies. In a next step, the porphyrin centers are filled by Zn atoms and ligands are used that can bind to the Zn. A ligand called DABCO (diaza-[2.2.2]-bicyclooctane) is admitted. Repeating the experiment, again, ongoing aggregation is observed, but this time the domains show linear features. Zooming into these lines reveals a substructure that can be most plausibly explained by interconnection of the porphyrin disks through the ligand. This gives rise to stack formation, thus the molecules adsorb in an edge-on orientation. In a parallel step, an alternative ligand molecule called BIPY (4,4'-bipyridine) was admitted. Face-on adsorption is observed. This is compatible with the larger size of this ligand, that prevents stacking [15]. This suggests, the supramolecular architecture, including its functionality, being switchable. This molecule is large 6 nm and we imaged up to 9 nm thick porphyrin wheels with molecular resolution.

Bio-molecules

With increasing molecular size – towards bio-molecules – it becomes impossible to use scanning tunneling microscopy. Then, another SPM variant, the atomic force microscope (AFM) is a good choice. This type of microscope does not rely on an electric current but on local forces, that originate, among other, from Van der Waals, electrostatic, and magnetic interaction. The tip is mounted on a cantilever that bends, or is driven into oscillation. A light pointer is used to monitor the deflection, that gives the force (gradient). That way, it is possible to image tissue, for instance, cellulose. Using a magnetic probe it is possible to image the domain structure of the tracks on harddisks and magnetically structured materials. Currently, the AFM does not yet yield similar high resolution in media than STM, and too little is known about the contrast formation.

Thick proteins adsorbed on surfaces are probed and molecular forces are measured. We studied adsorption of proteins, like actin (cytoskeleton), ATPsynthase (energy conversion), ferritin (iron storage), and the nucleic acids DNA and RNA (genetic information and translation). Sub-molecular contrast is hard to achieve when the molecules do not take an ordered structure. Yet, we are using commercial AFMs and tips.

One of the challenges is to prepare very smooth layers, that neither bind the nucleic acids too strong nor to weak. For this purpose we use organic molecules, exhibiting positive charges. Figure 12 shows an AFM topography of DNA. The molecule is imaged with an apparent width of 5 nm, what is 2.5 times larger than the nominal size. This is due to the fact that the probe measures an envelope of constant force gradient, and to limited resolution. These images have been taken in the so-called dynamic mode, when the cantilever is driven into oscillation, and the frequency shift due to the force field of the sample is used for feedback. This mode is gentle and the molecules are not moved by the probe. However, the adsorption is weak. Molecules move upon rinsing and blowing, the final steps in preparation. We observed pinning of very long DNA, that has aligned during preparation. We hope to be able to achieve optimal fixation, that still allows to visualize the interaction of specific proteins with nucleic acid on line, and to measure specific forces.

First experiments have been performed in collaboration with biophysical and organic chemists. This figure shows so-called rotaxane. A rotaxane is an axle, the

DNA, with a ring threaded around it. There is no chemical interaction between the axle and the ring such that the ring could over the DNA. When under control, this will represent an element of nanotechnology machinery.

Future

There are amazingly many questions to address by scanning probe microscopy, towards nanotechnology. I shall increasingly use the overlap zone between soft matter, hard matter, and scanning probe, such that we can produce, nanoscopically characterize, and manipulate hybridic nanosystems, at the same time. This aims at solid-biological interfaces of future nanodevices.

Realization will also be a matter of funding and recruitment of skilled young scientists. To educate pupils and students in nanoscience and -technology a bachelor profile has been created [16].

We make efforts to raise funding on regional, national and international level to advance scanning probes, and enhance applicability. The flagship Advanced Nanoprobing within the dutch nanotechnology initiative (NanoNed) is going to be put to sea. The project Nano*Lab* aims to facilitate and intensify regional collaboration. The project Advanced Scanning PRobes for Innovative Nanoscience and Technology (ASPRINT) joins together European expertise in scanning probe development. I do not believe that nanotechnology will become dangerous for us. I am most afraid of increasing bureaucracy and strictness of rules.

Mileva

Timed with the upcoming centenary of the 'Annus Mirabilis', 2005 is declared as the 'World Year of Physics' The aim is to bring the excitement of physics to the public and inspire a new generation of scientists. 1905 Albert Einstein published the work on the special theory of relativity. The contribution of Mileva Maric, his first wife, is controversially discussed [17]. There should be no doubt that she was a gifted mathematician and physicist, and contributed substantially developing their theory. This should make women concerned with physics, and feel self-confident. Society, industry, and academia will benefit from more female physicists being attracted. Also, scientists, together with media, have to work further, that physics and exact sciences will recapture a position in education and society, that measures up the real chances and benefits.

Closing

Time to thank a number of people who contributed to my development to this point. First, I thank the Subfaculteit Natuurkunde, the Faculty of Science, and the College van Bestuur, for appointing me to professor.

Many people gave more or less direct impulses to my carrier.
My supervisor in Osnabrück, Professor Werner Heiland allowed me to start an own group early.

I am in Nijmegen since two years now and I have to thank all members of our department for their contribution, and for creating such a pleasant atmosphere.
I hope we will obtain many exciting results, and have fun.
Riki Gommers, thanks to you, things cannot go wrong, worries disappear during our gezellige nederlandse conversation.

Hooggeleerde Rasing, Theo, my direct colleague, you helped me from begin on. Now, we are working together on big projects. Thanks to you I learned 'swimming' faster.

Hooggeleerde Van Kempen, Herman, my predecessor, I took over a prestigious lab, that was set up by you, over the years. I hope that I can make the best out of it.
Finally, I like to thank my family and friends. Mama, Papa, thanks for your care and interest, a fabulous childhood, and for being critical.

My husband, Hannes, this 'spagat' situation is unpleasant and we are looking forward living at the same place. Time is working for us. Thanks for your encouragement and confidence, despite of this complicated situation.

Fiona, it was too risky to have you here, you surprise me every day. Together we are strong.

Ik heb gezegd.

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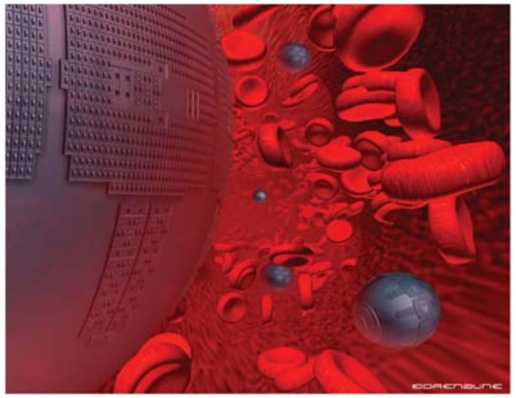
Figure 1: Artists view of respirocytes, nanorobot-based artificial erythrocytes, E-drenaline, Nanomedicine Art Gallery, www.foresight.org/Nanomedicine/Gallery/)



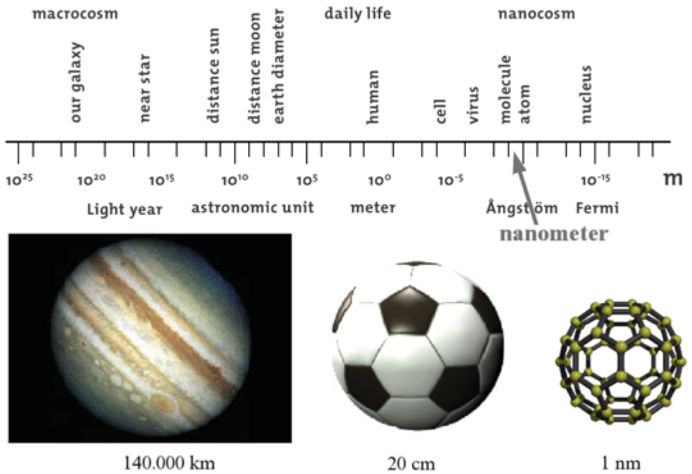


Figure 2: Scale of things and size relation

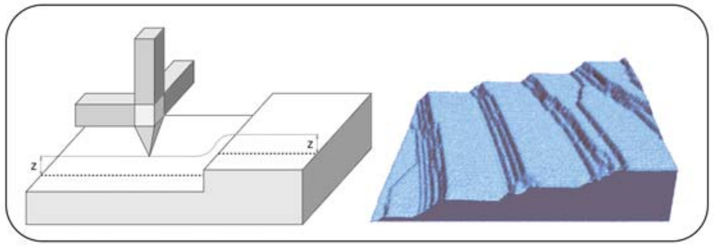


Figure 3: Scanning Probe Microscopy. Principle of Measurement.

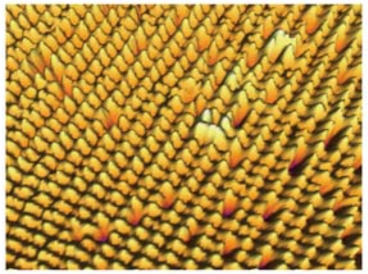


Figure 4: Scanning Tunneling Microscopy Topography of a platinum-tin alloy surface. The protrusions are measured on the platinum atoms, the tin atoms are invisible.

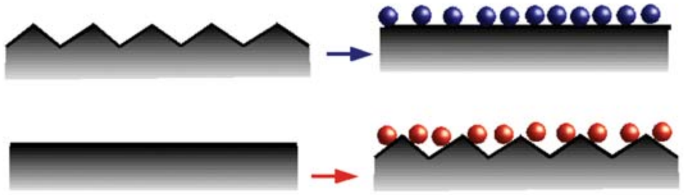


Figure 5: Deconstruction and reconstruction upon adsorption of electron accepting and electron donating species.

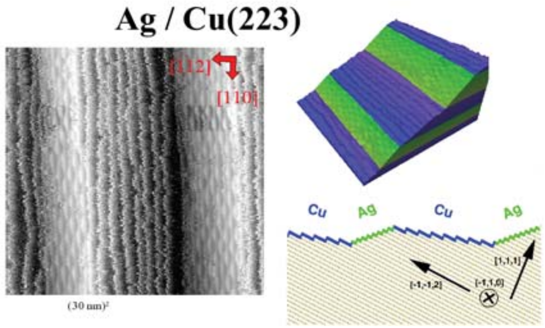


Figure 6: Nanostripes on a stepped Cu surface, A.R. Bachmann, et al, [11]

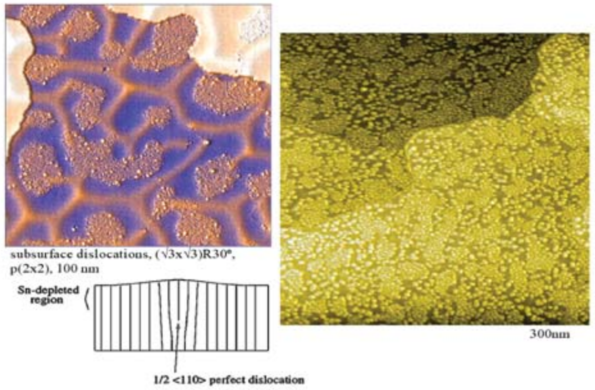


Figure 7 : Metastable phase of Pt3Sn(111) with subsurface dislocations. Directed cobalt islanding, M. Hoheisel

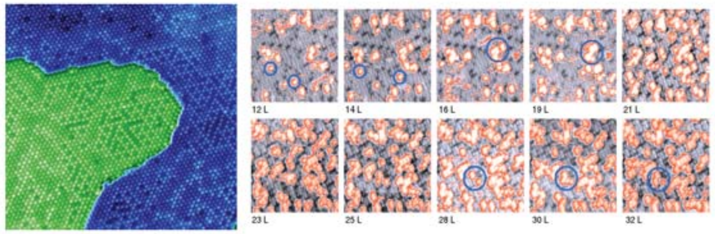


Figure 8: Left: STM topography of oxygen adsorbed on Pt3Sn(111), framesize 30 nm, exposure: 7000 Langmuir @ 800 K. Right: Sequence of STM topographies during adsorption of CO, showing mobility, 10 nm frames. The exposure is given in L(angmuirs), that is, 10^{-6} Torr times second. M. Hoheisel, et al.

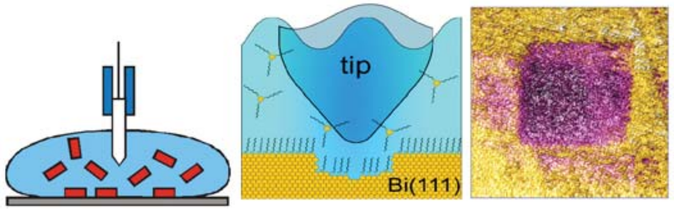


Figure 9: Liquid STM and nanomachining of Bi(111), framesize 500 nm, B. Hulsken.

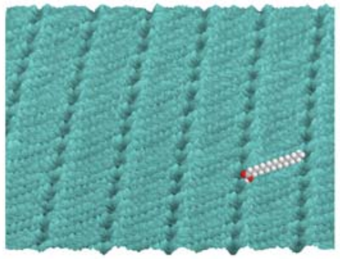


Figure 10: Self-assembled stearic acid layer on graphite, J.W. Gerritsen.

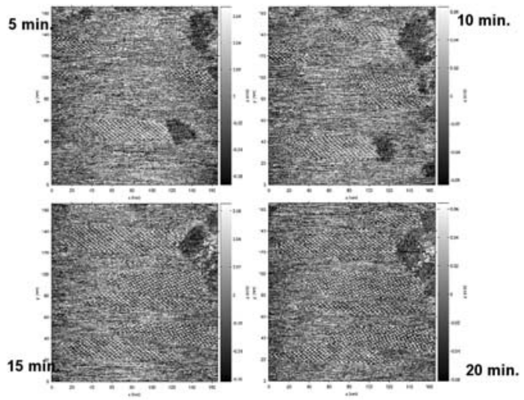


Figure 11: Sequence of STM topographies showing ordering process of prophyrin hexamer supermolecules, JAAW Elemans.

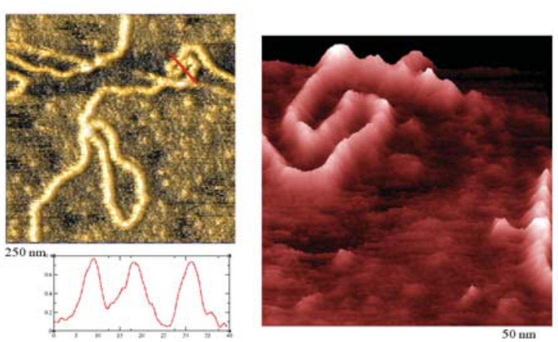


Figure 12: Atomic Force Microscopy Topography of DNA, P. Schön.